

Life study of a PBI-PEM fuel cell by current distribution measurement

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Abstract PBI-based polymer electrolyte membrane (PEM) fuel cells have short durability comparing with Nafion ones. It is known that the presence of phosphoric acid accelerates catalyst sintering, and the polymer is susceptible to getting degraded via oxidative degradation. However, the influence of the current distribution on the degradation process has not been investigated. In this work, current distribution was measured continuously during a steady state life test that was performed in a 50-cm² PBI-PEM fuel cell. The membrane-electrode assembly was prepared using techniques that are supposed to ensure satisfactory reproducibility at global level. Two different stages, i.e., activation and degradation, were identified. They show disparities in both global and local performance. It was found that the current distribution map is very heterogeneous, with variations around $\pm 50\%$ with respect to the average value during the whole lifetime of the cell. The non-uniformity of the current profile increases during the degradation, but it cannot be concluded that the current density distribution contributes to the short lifetime.

Keywords Current distribution · PBI · Durability · Fuel cell · Degradation

1 Introduction

Fuel cells are a solid alternative to combustion engines, turbines, and even small batteries used in portable applications. They achieve higher electric efficiencies and can transform chemical energy from different fuels, among which hydrogen is the most suitable, as it can be obtained from renewable sources. Therefore, this electrochemical device can play an important role in a hypothetical energy paradigm change to finish with the actual dependency on fossil fuels.

Because of their versatility, PEM fuel cells seem to be the most interesting fuel cell type and are subject of investigation. Lately, with the intention of operating at higher temperatures and profiting from all the consequent advantages, possible substitutes to traditional Nafion electrolyte have been studied. Polybenzimidazole (PBI) doped with H₃PO₄ is a good candidate and has attracted the attention of many of the researchers devoted to this topic. Short lifetime is one of the problems to be solved for PBI-based PEM fuel cells, and authors suggest a number of different reasons for the fast degradation. The origin of the performance decay seems to lie in two processes. One is the catalyst agglomeration, enhanced by the high electric potential in the cathode and the necessary presence of phosphoric acid and oxygen [1–3]. The second is the oxidative degradation of the polymer [4, 5]. Corrosion of the carbon support and loss of ionic conductivity due to H₃PO₄ dehydration at high temperatures [6] are other reasons mentioned in the literature. The advantages that working at temperature higher than 125 °C involves push researchers to find a solution. The investigation on modified membranes [7] and on alloy catalysts [8] is the main research line to overcome the problem. For low-temperature PEM fuel cells, a non-uniform current distribution is also investigated as a cause for low durability. This is usually related to a bad water management

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[9], which leads to a malfunctioning of certain regions of the membrane-electrode assembly (MEA). To the authors' knowledge, the effects of the current distribution on a PBI-based PEM fuel cell durability have not been studied. Current distribution measurement enables deeper analysis than the conventional methods as, besides global information, data at a local level are obtained. This technique gives information at any moment about the current density profile that is being generated under the fixed operation conditions, which makes possible to detect and diagnose failures and to eventually associate them with the phenomena occurring inside the fuel cell.

In this work, current distribution measurement has been used as an experimental method to analyze the performance of a 50-cm² high-temperature PBI-based fuel cell during its whole lifetime. The main goal was to assess the uniformity of the current distribution and to determine if it is connected to the degradation of the system. To that end, the MEA was prepared using a non-modified PBI membrane and a conventional Pt/C catalyst, so the lifetime is expected to be short. The catalyst was deposited using the manual spray method, which is one of the most commonly used and supposed to ensure a reasonable reproducibility in global performance.

2 Experimental methods

2.1 Preparation of the MEA

The catalyst (E-TEK 40 wt% Pt on carbon Vulcan XC-72) was deposited over a Vulcan XC-72-based microporous layer using the manual airbrushing technique, the Pt load on each electrode being 0.25 mg cm⁻². Graphite paper (TORAY TGPH-90) was used as gas diffusion layer (GDL).

As for the polymer electrolyte, a PBI membrane which had been casted from a PBI solution synthesized from its monomers [10] was doped with H₃PO₄ by immersion in a 75 wt% phosphoric acid bath. Doping level acquired by the membrane was around eight molecules of acid per polymer repeating unit. Afterward, the membrane was taken out, wiping off the excess of H₃PO₄. To complete the assembly, the doped membrane was sandwiched between the two electrodes, hot-pressing the whole system. Once the MEA was ready, it was immediately inserted into the cell.

2.2 Experimental protocol

The steady state life test presented in this work consisted mainly in the operation of the fuel cell at a constant potential of 600 mV while the average and local current density values were recorded. Additional electrochemical

tests were performed daily to acquire global information about the performance of the different components of the cell. These tests included polarization curves, cyclic voltammetry, crossover measurements, and electrochemical impedance spectra (EIS). Cyclic voltammetry experiments were carried out at operating temperature by purging the cathode side with 100 sccm humidified N₂. The cathode was the working electrode, while the anode acted as both counter and reference electrode. Crossover measurements were performed under the same conditions and fixing a constant potential of 500 mV until the current density was stable.

The E–I pairs were controlled and measured by a potentiostat/galvanostat Autolab PGSTAT (Ecochemie, The Netherlands) together with a 20 A booster. Local current measurements were performed by a sensor plate formed by 100 sensors (S++, Germany) placed on the cathode side. Each sensor quantifies the total current flowing through a 0.5-cm² isolated segment. This device also allows to measure the temperature distribution. Neither the MEA nor the end plates were modified at all to perform the current distribution measurement. The only difference with respect to the usual operation was the placement of the sensor plate behind the flow field plate (2 mm thickness) of the cathode side. Pros and cons of this measurement technique were discussed in ref. [11].

The cell was operated at 423 K and ambient pressure. Pure oxygen and hydrogen were fed to the cathode and anode at 100 sccm.

3 Results and discussion

When the MEA was inserted into the cell, the working potential *E* was set to the operating value and the current density was continuously registered. No starting protocols were put into practice.

Figure 1 shows the average current density produced by the PBI fuel cell when operating at *E* = 600 mV during the life test.

A first stage lasting about 35 h in which the fuel cell performance improves can be observed. This period is usually called activation, conditioning or break-in and is believed to be mainly related to the redistribution of H₃PO₄ over the catalyst active sites. The electrolyte penetration in the catalyst layer increases the number of sites where proton transport is possible and thus the reaction zone is extended. This process is supposed to be quick [12] and probably responsible for the initial steep performance improvement. The removal of impurities and membrane humidification are among other causes to bear in mind [13]. Afterward, a stage characterized by a continuous performance decline is observed. The phenomena that

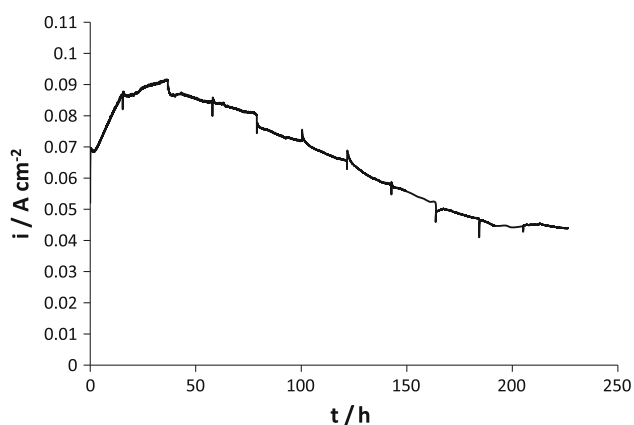


Fig. 1 Evolution of the average current density during the lifetime of the fuel cell at $E = 600$ mV

originate the fuel cell degradation occur from the beginning of operation, but their effects on the global performance are only noticed when the activation is mitigated.

An issue to be discussed is the short life of the fuel cell. It is usually accepted that the rated power degradation at the end of life should be $<10\%$ [14]. In this experiment, the average life (hours to 10 % average current density decay) would be 130 h if the initial performance is considered. A longer and more stable operation can be observed in some other durability studies for PBI fuel cells [1–3, 15], probably due to the use of membranes synthesized under more controlled protocols or commercial ones. As stated in the previous sections, the presence of H_3PO_4 and higher operating temperature is the most plausible thesis that explains the short life reported for PBI-based

fuel cells. In this case, the absence of fillers or modifications allows a higher H_3PO_4 mobility and leads to an accelerated degradation of the system. This made possible to evaluate if there is any influence of current distribution on the lifetime of the fuel cell in shorter times, as phenomena that cause fuel cell failure take place faster. This hypothesis is supported by another work from the same authors in which an improvement of fuel cell stability and performance is achieved when using modified PBI membranes [16]. The shorter than usual duration of the conditioning stage in this work is also consistent with a higher acid mobility.

To study the evolution at local level is of interest, as the differences that can be found in the performance of the different electrode regions can indicate possible causes for the global behavior. Figure 3 shows the changes in the local current density during the experiment for the 16 divisions depicted in Fig. 2a. In Fig. 2b, c, the flow channel geometry is also shown. Although the spatial resolution is 0.5 cm^2 , the individual analysis of 100 segments would be excessive. Therefore, the segments were put into 16 groups (divisions) to simplify the discussion of the results. The current density shown for each one of the 16 divisions is the average current density of the segments included in the region (division) in question. All the regions follow the conditioning-degradation behavior noticed for the average current density, coinciding also in the duration of each stage. Another point to be highlighted is that each sector generates a different current density, which proves certain non-uniformity. In addition, most curves are not parallel, meaning that the improvement rates during the activation

Fig. 2 **a** Numbering of the different divisions (regions) of the electrode; see text for discussion, **b** scheme of the gas flow in the cathode side, **c** scheme of the gas flow in the anode side

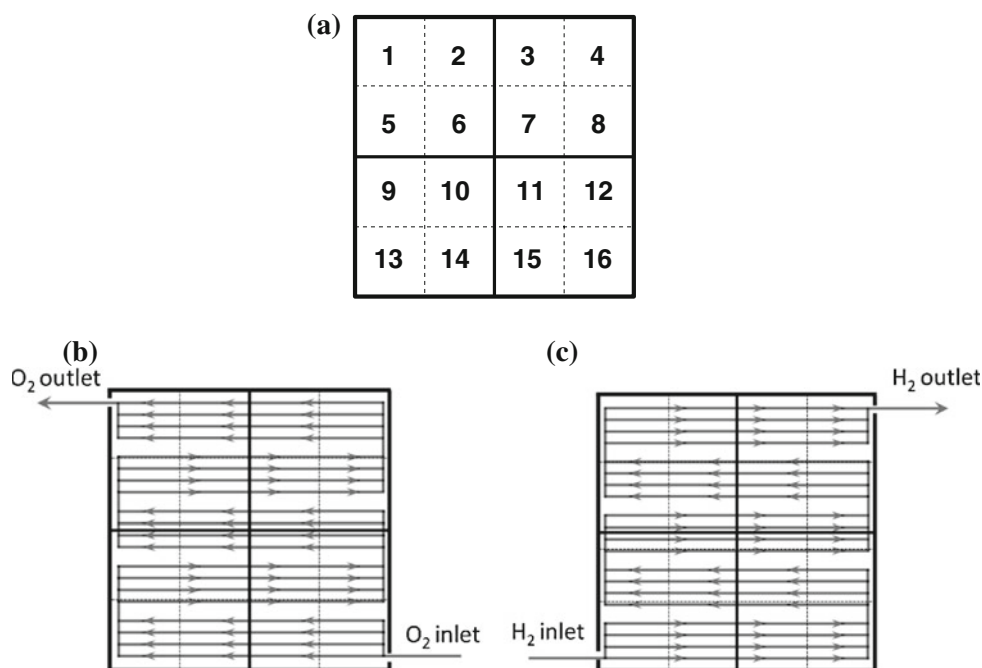
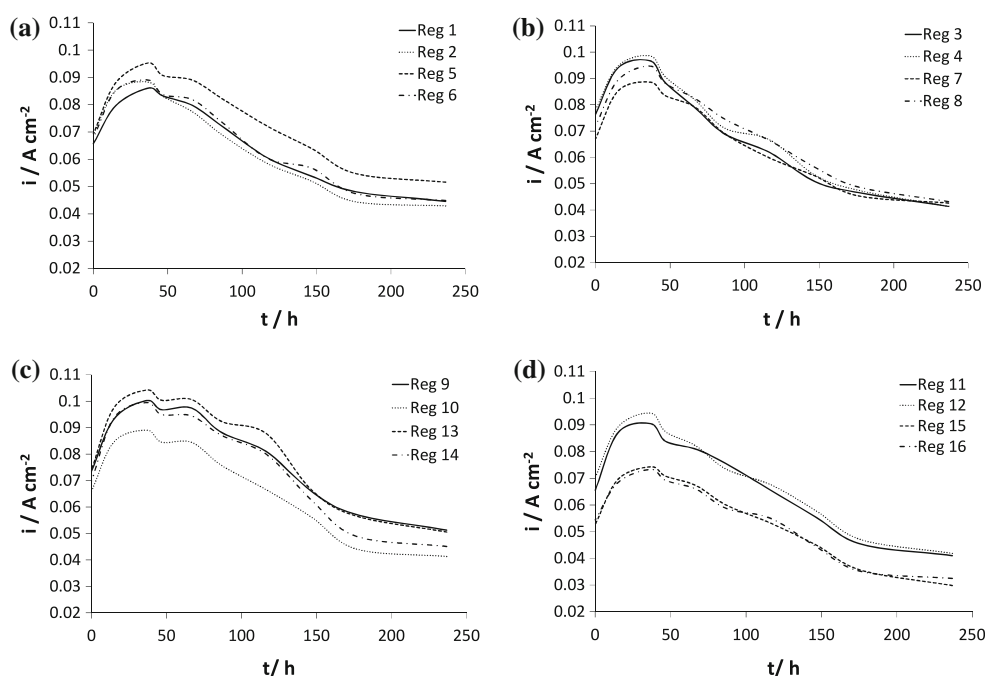


Fig. 3 Evolution of local current density in Regions **a** 1, 2, 5, 6 (*top left quadrant* of the electrode), **b** 3, 4, 7, 8 (*top right quadrant* of the electrode), **c** 9, 10, 13, 14 (*bottom left quadrant* of the electrode), and **d** 11, 12, 15, 16 (*bottom right quadrant* of the electrode)



period or the degradation rates are different for each zone. These aspects are important and susceptible to being more carefully analyzed.

The non-uniformity of the current density is not inherent only to the first times after potential application, as differences between regions exist until the end of the experiment. In order to quantify the heterogeneities, the relative standard deviation (RSD) of the average current density, on the basis of the local current densities of the different 100 segments, was calculated at different times. Figure 4 shows that, during the activation, RSD values do not vary significantly so it can be stated that the mean deviation of the current density with respect to the average value remains almost constant throughout this period.

Figure 5 presents the current distribution maps during the activation stage, expressed as relative difference of the current density with respect to the average value. The maps have been drawn using the full spatial resolution (100 segments) and contoured to eliminate abrupt gradients. A grid has been included to divide the surface into the same 16 regions that will still be used for discussion purposes. At the beginning of the study ($t = 0$ h), Regions 3, 4, 9, and 13 are the most active, whereas 15 and 16 produce the lowest current density. This map confirms that the current distribution is not even, and heterogeneities are indeed substantial, since current density deviations of $\pm 50\%$ with respect to the average value can be found. To explain this, the effects of the reactant concentration should be discarded, as the cell is operated at least at a stoichiometry of 3 for hydrogen and 5 for oxygen, which can be considered enough to neglect mass transfer limitations. Moreover, as it

was proved in [11, 17], when concentration effects are important, current distribution maps follow a clear trend according to the concentration profile of the limiting reactant, which is not the case. In Fig. 2b, c, the flow channel geometry is schematized. Gases follow a quadruple serpentine in both anode and cathode sides, so if lack of reactant existed, a decreasing current density gradient obeying the flow direction would be expected. For a conventional PEM fuel cell, current distribution heterogeneities may have to do with liquid water profile in the membrane, as its proton conductivity dramatically depends on the water content. Nonetheless, the conductivity of PBI is only slightly influenced by the presence of water and then a possible non-uniform distribution does not seem to

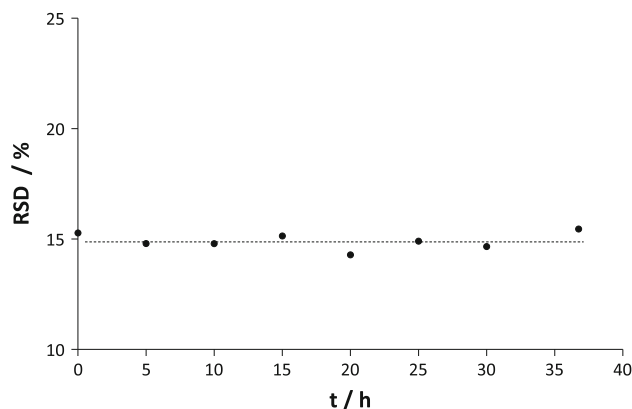


Fig. 4 Relative standard deviation (RSD) of the average current density at different times during the activation period

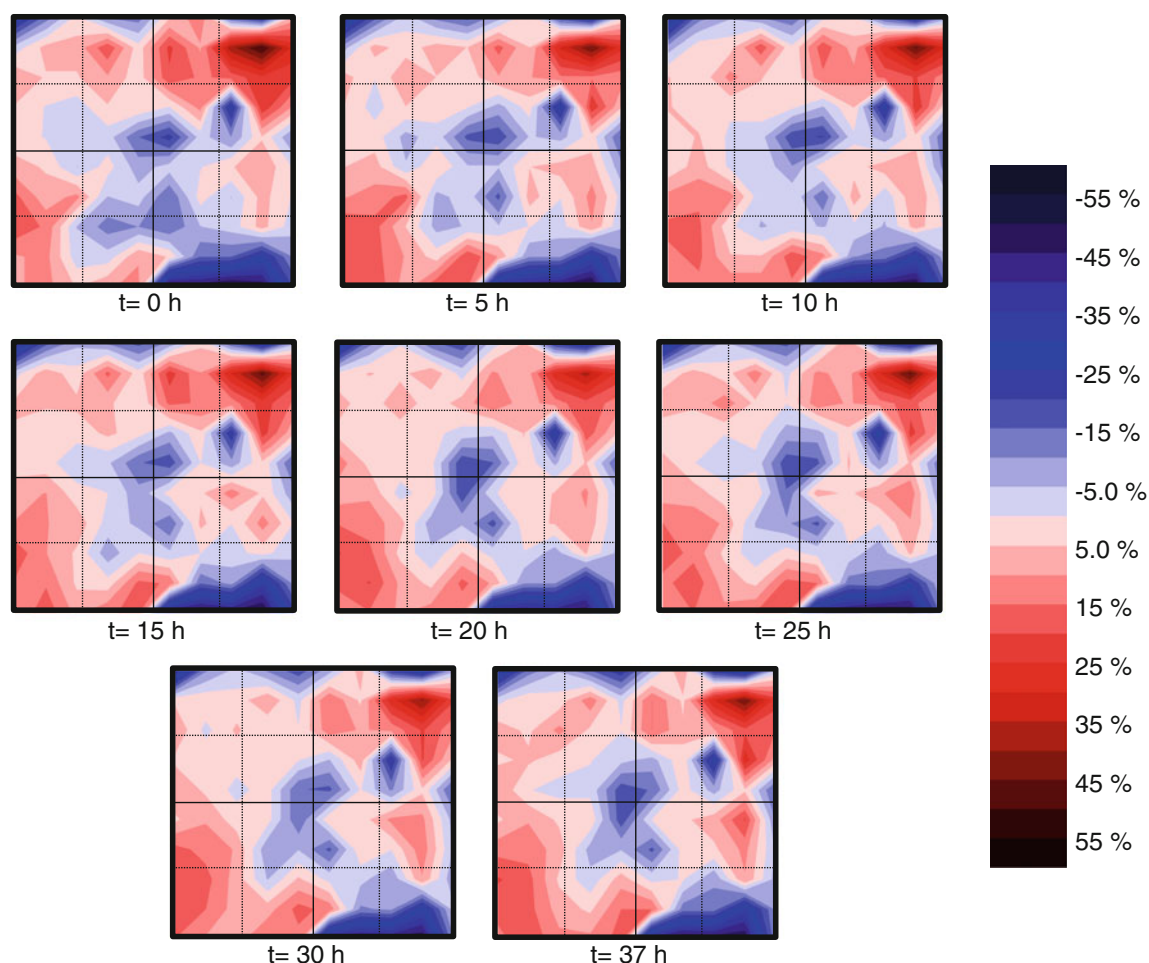


Fig. 5 Relative difference of the current density with respect to the average value at different times during the activation stage

be a suitable justification for such a heterogeneous current density map. Temperature distribution was also measured during the experiment, being always almost uniform and showing deviations of only ± 1 K with respect to the operating temperature in disseminated segments. The reasons might then be linked to electrode unevenness and more specifically to an irregular catalyst spread, despite the fact that a technique directed at achieving a good Pt distribution and reproducibility [18], which is widely used nowadays, was applied [19–21].

Since the current density produced by all the regions increases during the first 35 h, a decrease with time in the relative difference of one division means that it improves, but at a lower than the average rate, whereas an increase implies a more pronounced activation. Generally speaking, it can be concluded that the current distribution profile does not essentially change. Regions 3, 4, and 13 are more active from the beginning and keep their relative activity until the end of the break-in stage. On the contrary, Regions 15 and 16 have a poor performance during the

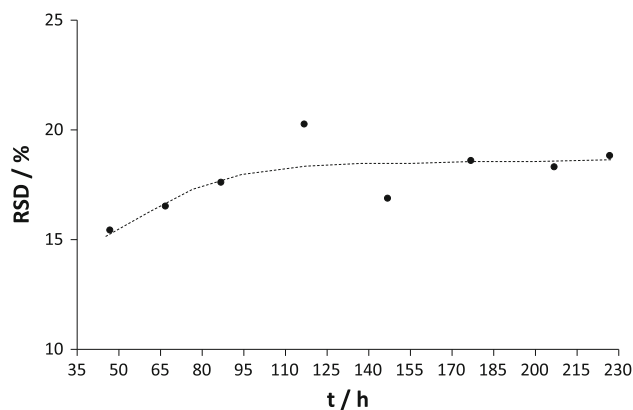


Fig. 6 Relative standard deviation (RSD) of the average current density at different times during the degradation period

entire break-in period. These regions are located close to the fuel outlet and inlet as well as to the oxidant inlet, but there is no evidence that their performance is related to their location. More experiments should be carried out to determine whether the position of inlets and outlets and the

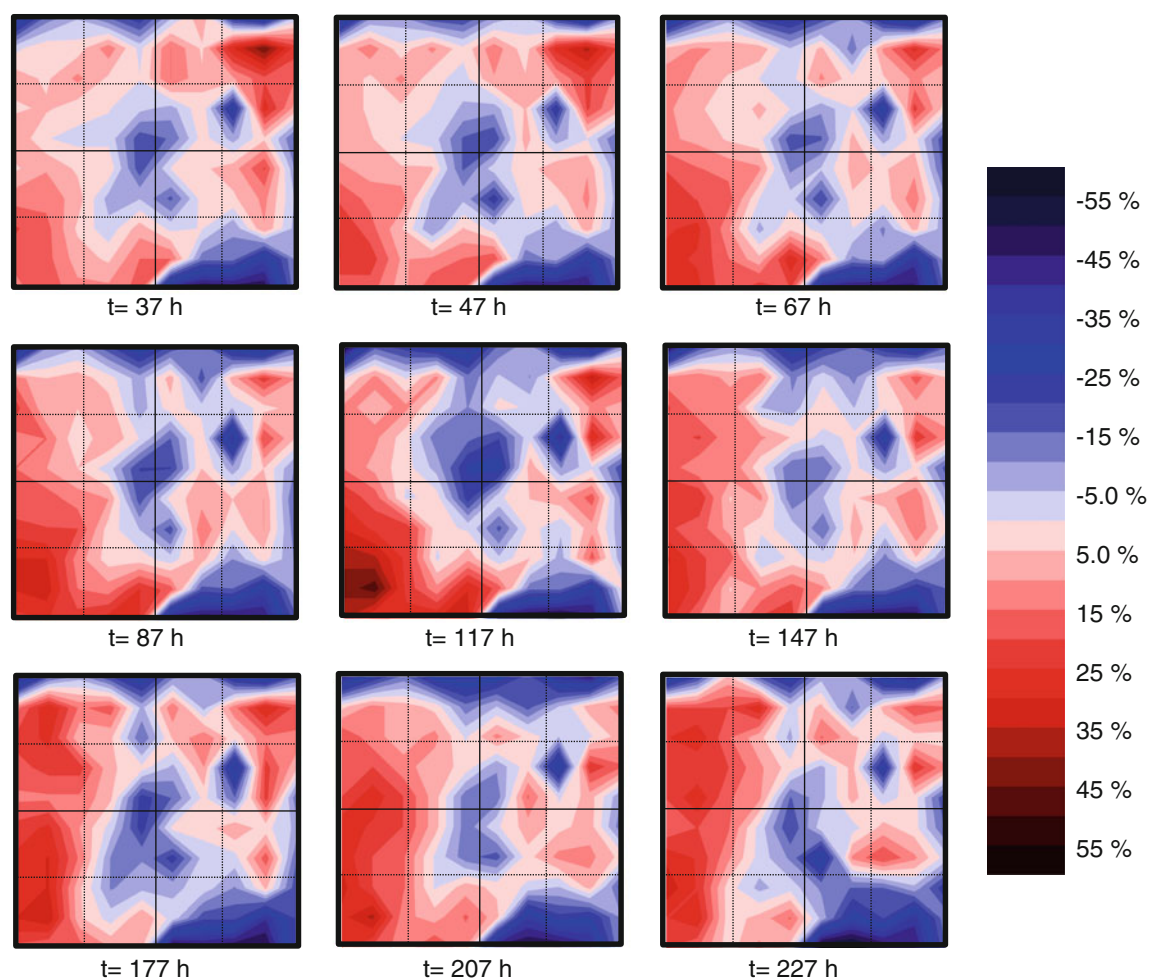


Fig. 7 Relative difference of the current density with respect to the average value at different times during the degradation stage

flow path of gases have an influence or not in the activation processes.

Figure 6 is similar to Fig. 4, and it aims at showing the changes in the current density at different times of the degradation stage. The tendency of the RSD to grow is apparent, increasing by more than 3 % at the final time (this means a relative growth of 21 %). Then, current distribution maps are even less uniform at the end of the lifetime than at the beginning, and the growth of the relative standard deviation seems to occur after the activation stage.

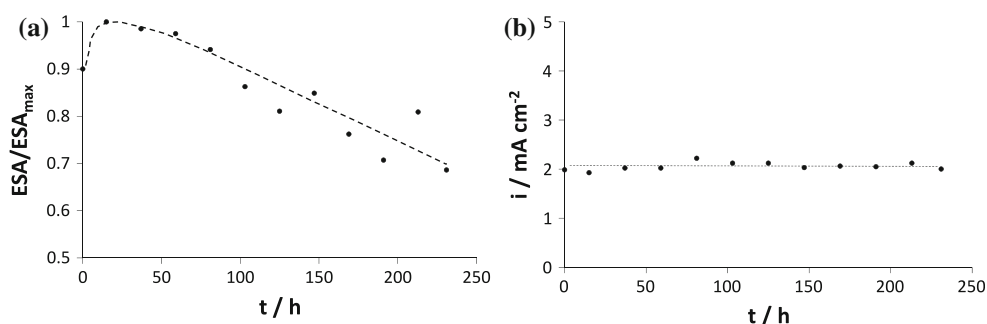
In the same way as Fig. 5, Fig. 7 shows the current distribution maps during the degradation stage. In this case, a decrease with time of the relative difference indicates a faster than the average degradation and an opposite evolution entails that the current produced in the division in question decreases more slowly. During this period, some changes in the current profile can be observed, as Regions 1, 5, 9, and 13, all located on the left side of the assembly, turn to a more red color. They present thus a less marked decay rate. Regions 15 and 16 slightly turn to dark blue,

and Regions 3 and 4 to pale red, denoting a little faster degradation. Pei et al. [22] presented a work in which different portions of MEA were analyzed after degradation. Their results indicate that the regions corresponding to fuel and oxidant outlets get more degraded, which is not in agreement with Fig. 6. Differences between degradation mechanisms of conventional and PBI-based fuel cells may be the reason for this disagreement.

Although not all the regions present exactly the same degradation rates, it cannot be concluded that the existence of current density inhomogeneity accelerates the performance loss phenomena. The degradation trends do not have a clear relationship with the regions that produce more or less current density. If the uneven current distribution was responsible for the short life of the cell, a strong link between decay rates and the performance of the different regions would be expected.

As mentioned, the two main reasons for the short PBI fuel cell durability is usually catalyst sintering and/or membrane oxidative degradation. To assess the catalyst

Fig. 8 **a** Changes in the electrochemical surface area of the cathode side during the life test. **b** Changes in the hydrogen crossover current density during the life test



sintering, Fig. 8a shows the changes in the electrochemical surface area (ESA) of the cathode catalyst during the life study. This parameter has been obtained by integration of the hydrogen desorption peak acquired from the cyclic voltammetry experiments performed daily to fuel cell. All the values were divided by the maximum ESA measured.

After the conditioning stage, during which the number of active sites increases, the ESA decreases notably with time, which is an indicator of loss of catalyst activity most likely due to agglomeration.

To evaluate membrane degradation, hydrogen crossover was measured. Figure 8b presents the variation of the current density caused by the hydrogen crossover through the membrane during the experiment. It can be seen that the current density measured does not suffer significant changes and always keeps acceptable values for PBI. This is a good indication for discarding membrane failure as a possible cause for MEA degradation. Therefore, catalyst particles coalescence should be pointed out as the main reason responsible for the PBI fuel cell short life and according to the current distribution information, this agglomeration apparently occurs over the whole electrode surface.

4 Conclusions

From this work, the following conclusions can be drawn:

- Despite the careful manufacture of electrodes, differences of $\pm 50\%$ of the local current densities with respect to the average current density value could be observed.
- During the life study, two stages could be distinguished. The initial one is characterized by an improvement of the fuel cell performance, whereas throughout the second one a continuous performance decrease occurs.
- After the activation stage, no relevant changes in the current density distribution could be detected. The relative difference in current density between regions of the electrode remains almost unchanging during this period.

- During the degradation stage, some changes could be observed. The RSD increased by 21 % with respect to its initial value. However, it cannot be stated that the short life of the cell is related to the uneven current distribution.
- Catalyst agglomeration is most likely responsible for the MEA degradation. The coalescence of Pt particles affects the whole electrode surface.

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